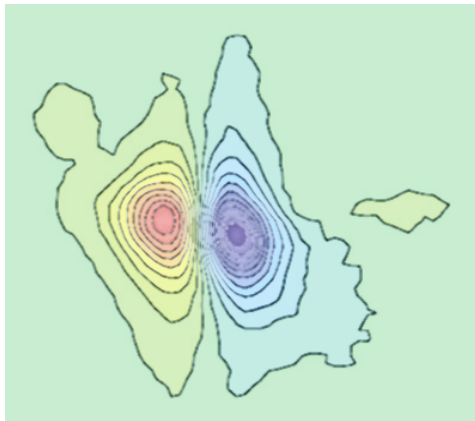


Advanced magnetic x-ray spectroscopies for the fine understanding of magnetic nanomaterials



Amélie Juhin (IMPMC, Paris)

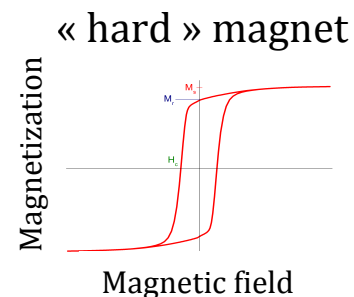
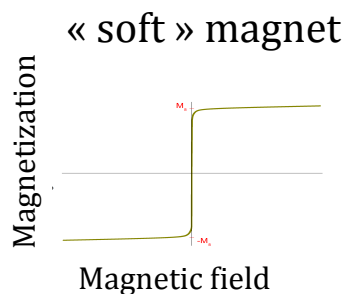
Outline

1. **Motivation** : bimagnetic nanoparticles and liquids
2. **Key ideas of hard x-ray RIXS-MCD**
3. **Example n°1** : interface quality in core@shell nanoparticles
4. **Example n°2** : magnetic anisotropies in core@shell nanoparticles
5. **Example n°3** : interparticle interactions in binary ferrofluids

Magnetic nanoparticles

Applications : magnetic recording, permanent magnets, biomedicine

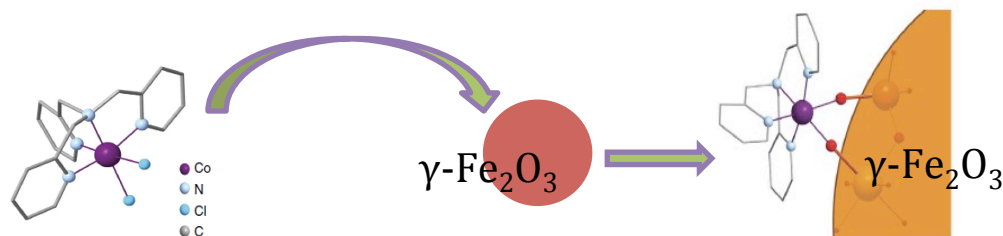
→ Tuning of size, shape, composition



bimagnetic core@shell strategies



functionalization by paramagnetic complexes



Prado et al, Nature Communications 6, 10139 (2015)

Open question :

How to tune at will magnetic properties through fine tailoring ?

Critical role of internal structure : thickness / composition / shape / interface quality
What role does each magnetic component play **in the coupled object** ?

Ferrofluids

Colloidal suspension of magnetic nanoparticles in a liquid carrier (water, oil)

- ferromagnetic material
- nanoparticle diameter in the 5-25 nm range

One particle = one magnetic dipole



→ magnetically driven macroscopic properties governed by magnetic dipole interactions

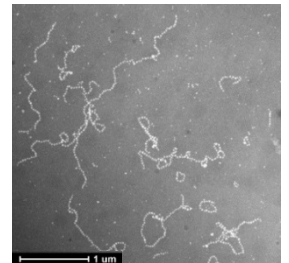
Applications: engineering (car dampers, seals), biomedical (hyperthermia, drug delivery)

Open questions :

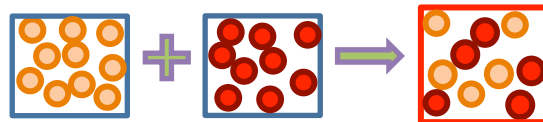
- **How to tune macroscopic magnetic properties through nanoscale dipole interactions ?**

targeted applications, novel magnetic responsive materials

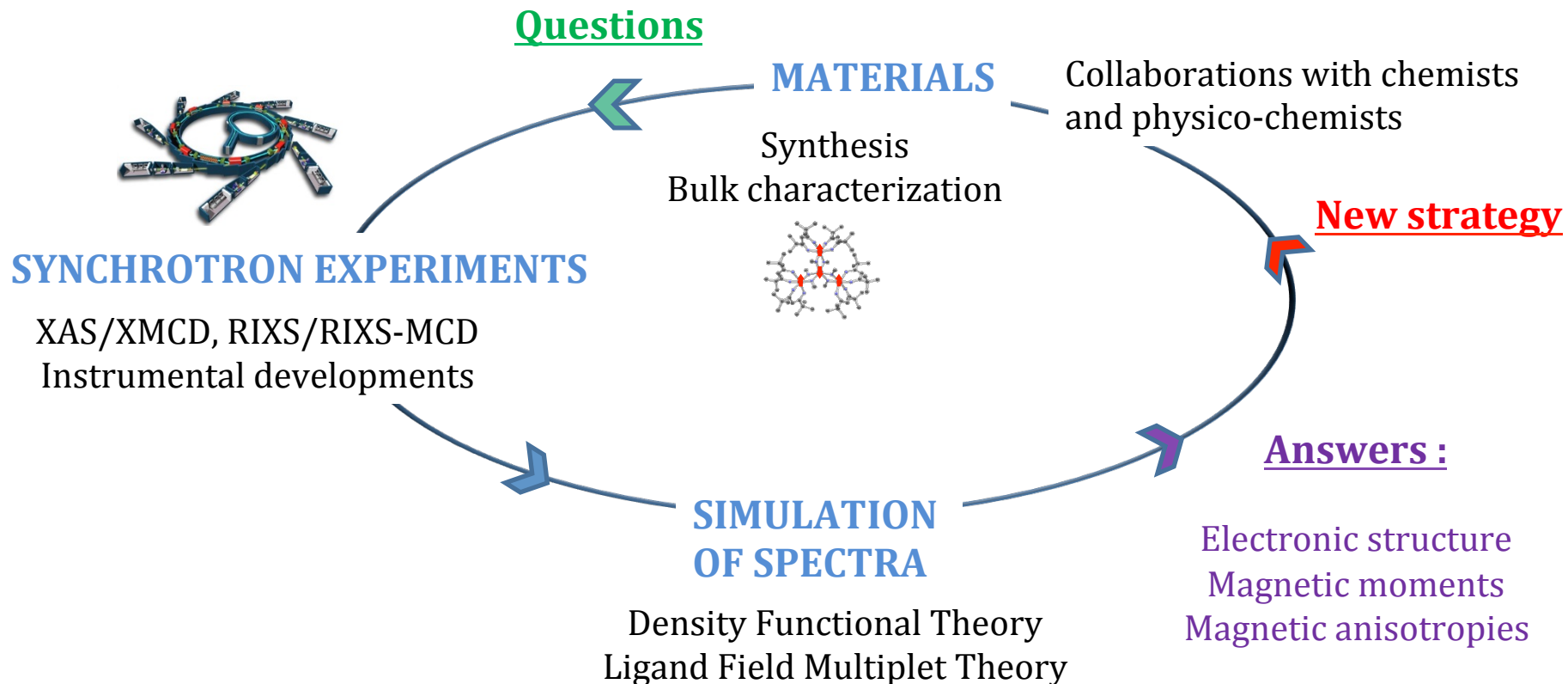
→ **How does self-assembly of nanoparticles influence magnetic properties ?**



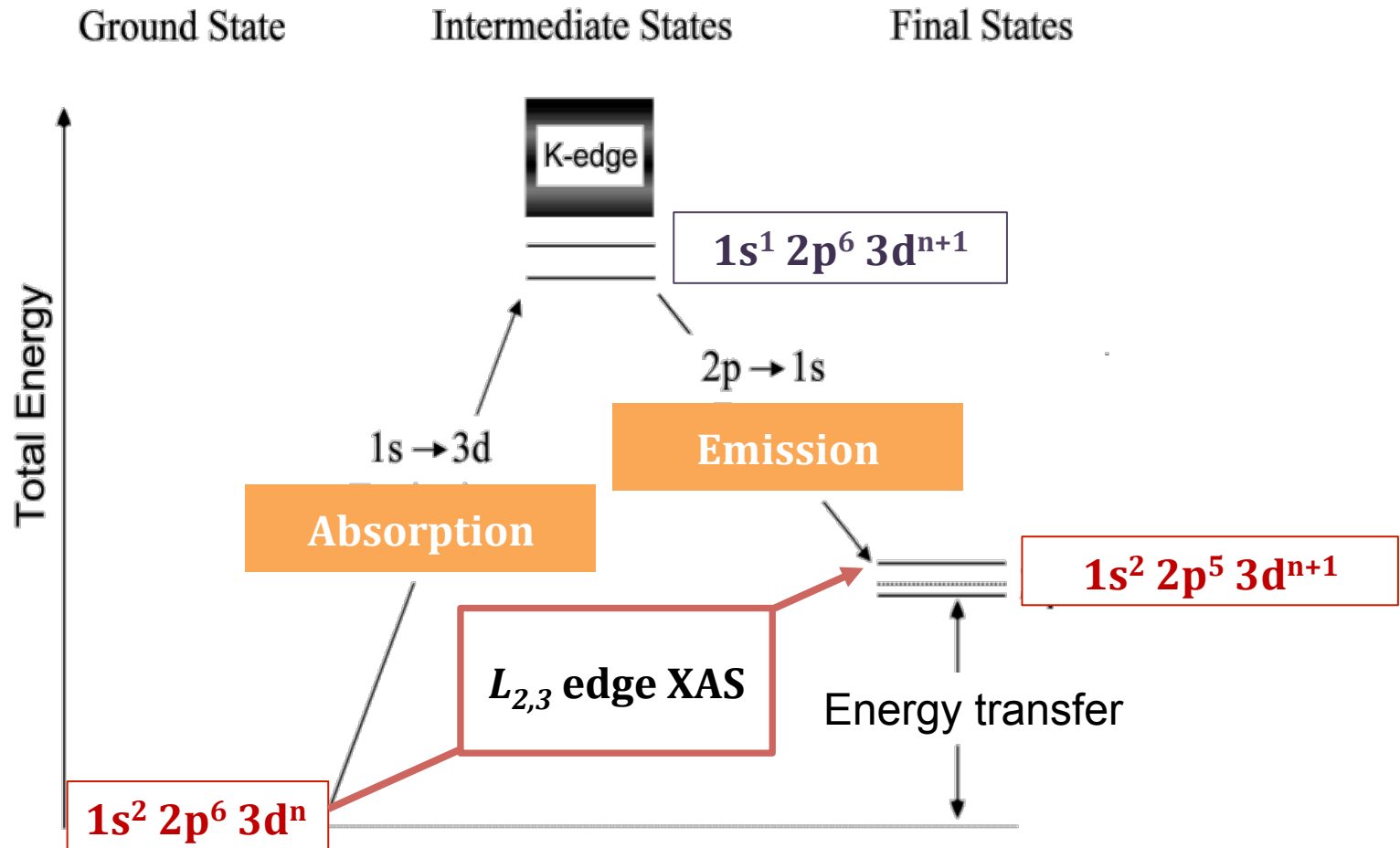
→ **Can binary mixtures build a new class of ferrofluids interesting for applications ?**



A combined approach



1s2p RIXS-MCD of 3d transition metal ions



***1s2p* RIXS-MCD : similar information as $L_{2,3}$ soft XMCD,
though using hard x-rays in and out**

For what questions and samples is hard x-ray RIXS-MCD useful for ?

Samples

All samples unsuitable for soft x-rays:

Multilayers, buried layers
Nanoparticles (> 5 nm)
Liquids
Systems under pressure

**MCD enhancement (x10) w.r.t. K edge XMCD
for ionic-covalent compounds:**

Oxides, molecular compounds...

Sikora, AJ, et al. Phys. Rev. Lett. 105, 037202 (2010)
ESRF Highlights 2010

Questions

Electronic and magnetic structure:

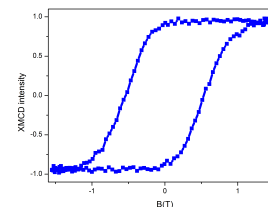
Spectroscopy measurements



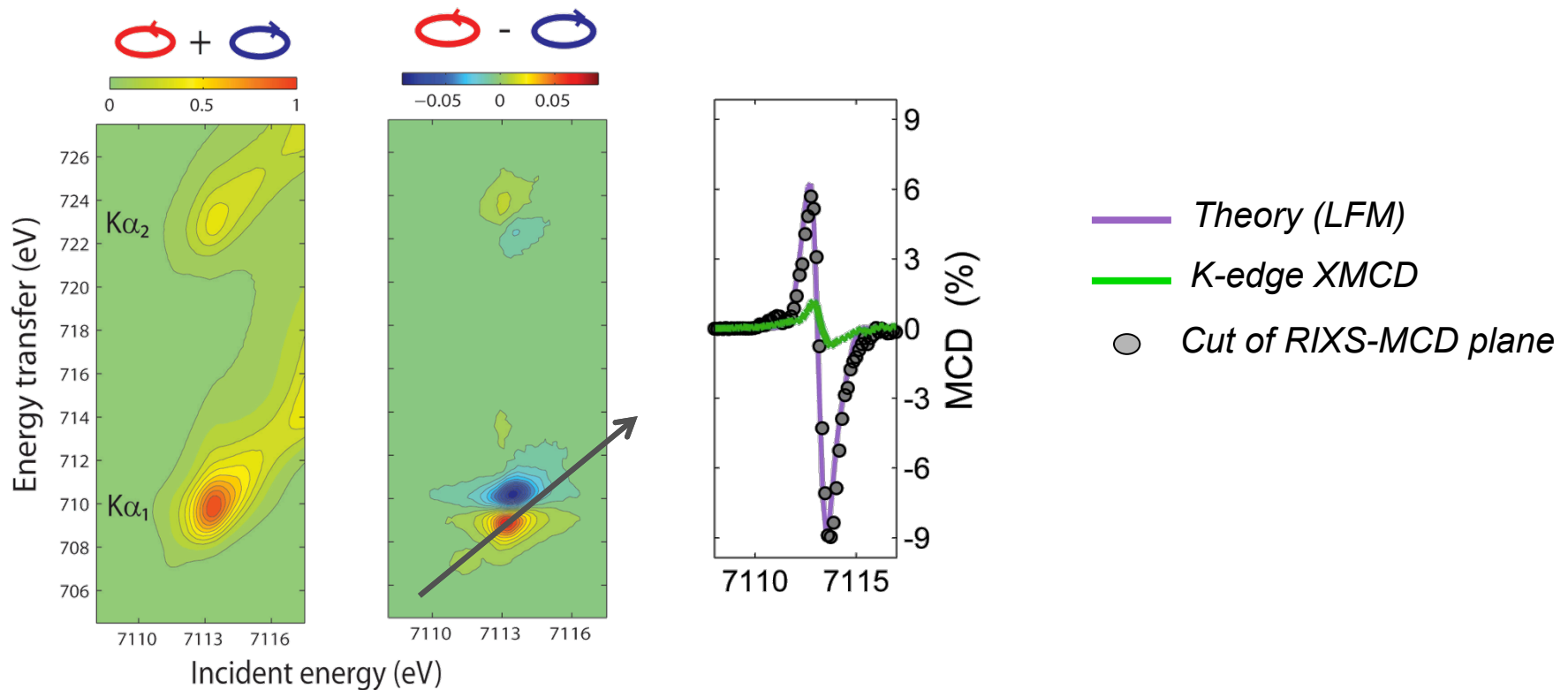
Valence, coordination,
magnetic moment

Magnetic anisotropies:

Magnetometry measurements



How does RIXS-MCD compare to *K*-edge XMCD ?



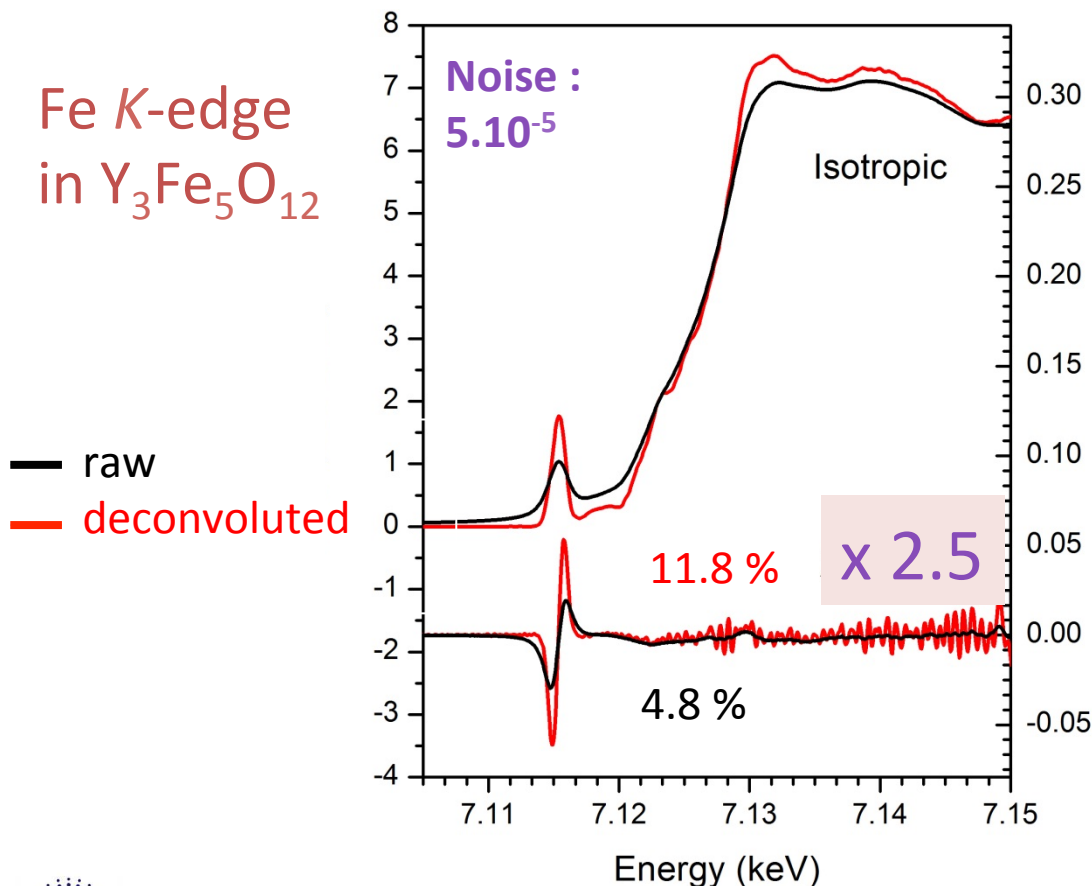
- Reduced lifetime broadening using RIXS detection
- MCD multiplied by 10 by comparison to Total Fluo. Yield detection

Is the intensity enhancement only due to the reduced lifetime broadening ?

Is the intensity enhancement only due to the reduced lifetime broadening ?

XMCD spectra measured in TFY with high signal-to-noise (average of 40 spectra)

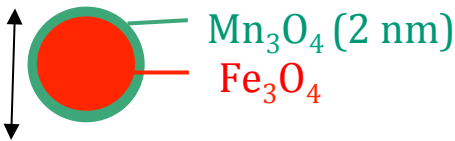
→ Partial deconvolution from $1s$ corehole lifetime broadening (GNXAS)



Reduction of lifetime broadening does only part of the MCD enhancement that is measured in RIXS

Example 1. Buried interface in core@shell nanoparticles

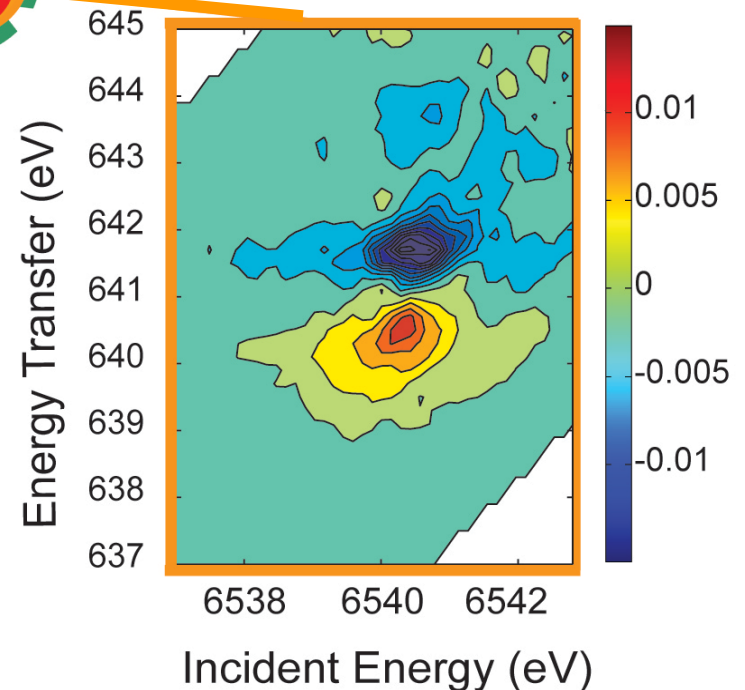
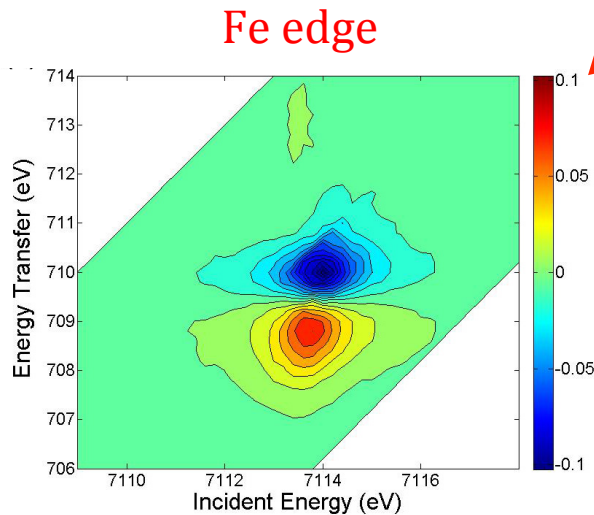
Targeted structure : ~ 13 nm



TEM-EELS :
no clear picture



$T_c(\text{Mn}_3\text{O}_4) = 43$ K
No RIXS-MCD signal at room T



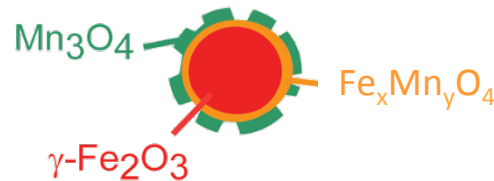
- no Fe^{2+}
- dominant $^{[4]}\text{Fe}^{3+}$

- direct evidence of an interdiffused layer
- dominant $^{[4]}\text{Mn}^{2+}$

Example 1. Buried interface in core@shell nanoparticles

→ Proposed quantitative model for the internal structure

$$0 \leq \text{Fe}_2\text{O}_3 \leq 5.0 \text{ nm} \leq (\text{Mn,Fe})_3\text{O}_4 \leq 6.1 \text{ nm} \leq \text{Mn}_3\text{O}_4 \leq 6.4 \text{ nm}$$



→ Quantitative understanding of measured bulk magnetic properties

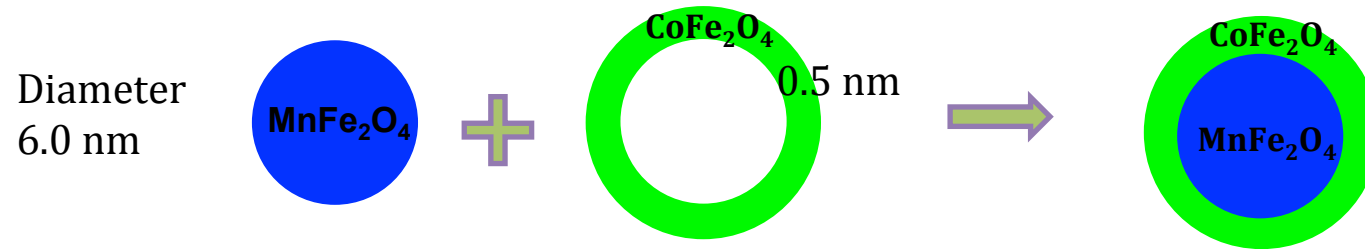
$$M_s (\text{model}) = 46 \pm 5 \text{ emu g}^{-1} \text{ vs } M_s (\text{SQUID}) = 43 \text{ emu g}^{-1}$$

Comparison to similar core@shell particles with sharper interface

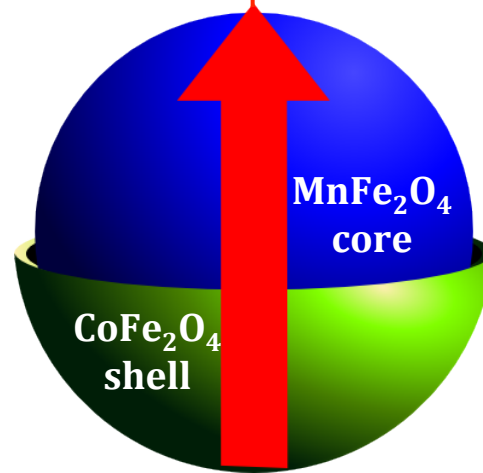
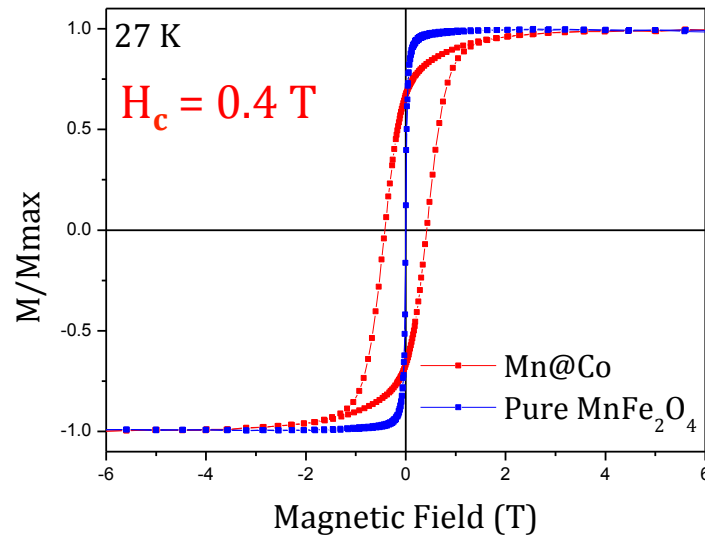
↓
higher magnetic coercivity, lower T_B

We established a direct relation between magnetic properties and the interface quality

Example 2. Magnetic anisotropies in bimagnetic core@shell particles

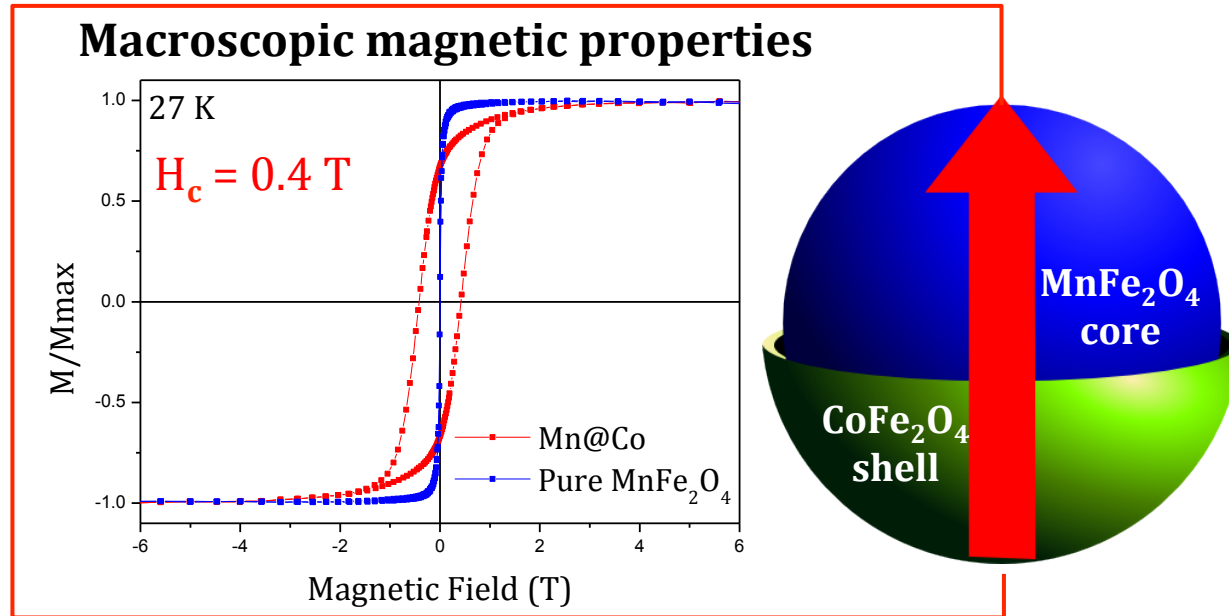


Macroscopic magnetic properties



Bulk magnetometry provides an average image

Example 2. Magnetic anisotropies in bimagnetic core@shell particles



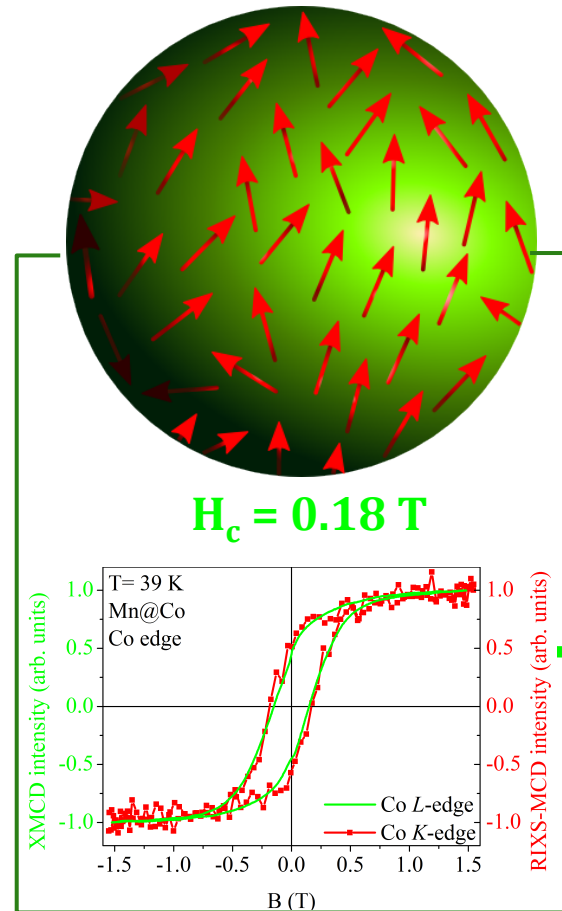
What are the magnetic contributions of the core and the shell?



- Hard X-ray RIXS-MCD and soft X-ray MCD → bulk and surface sensitive information
- Co edge vs Mn edge → disentanglement of Co-bearing and Mn-bearing components

Example 2. Magnetic anisotropies in bimagnetic core@shell particles

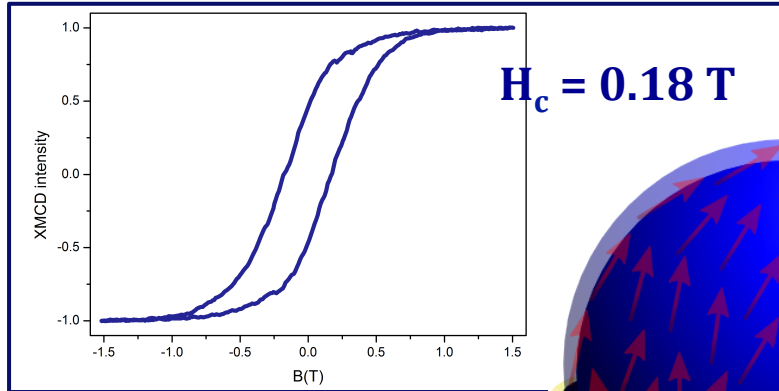
CoFe₂O₄ shell
XMCD detected
magnetization curve



XMCD/RIXS-MCD at the Co edge:

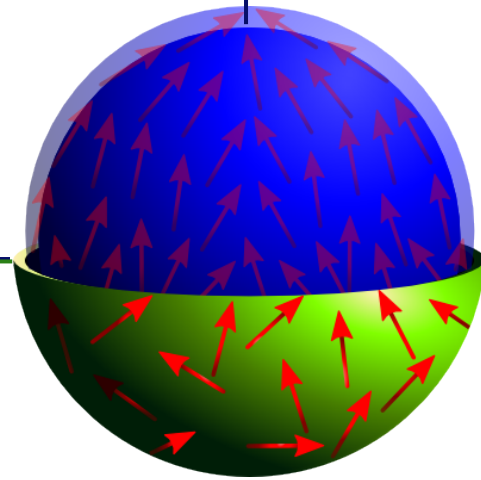
probes the Co in the top 0.5 nm
with **soft X-rays**
and with **hard x-rays**

Example 2. Magnetic anisotropies in bimagnetic core@shell particles



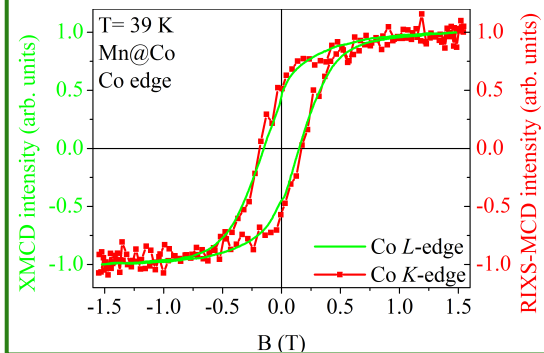
MnFe_2O_4 core external layer
XMCD detected curve

Soft XMCD at the Mn $L_{2,3}$ edges:
probes the Mn in the top 2 nm

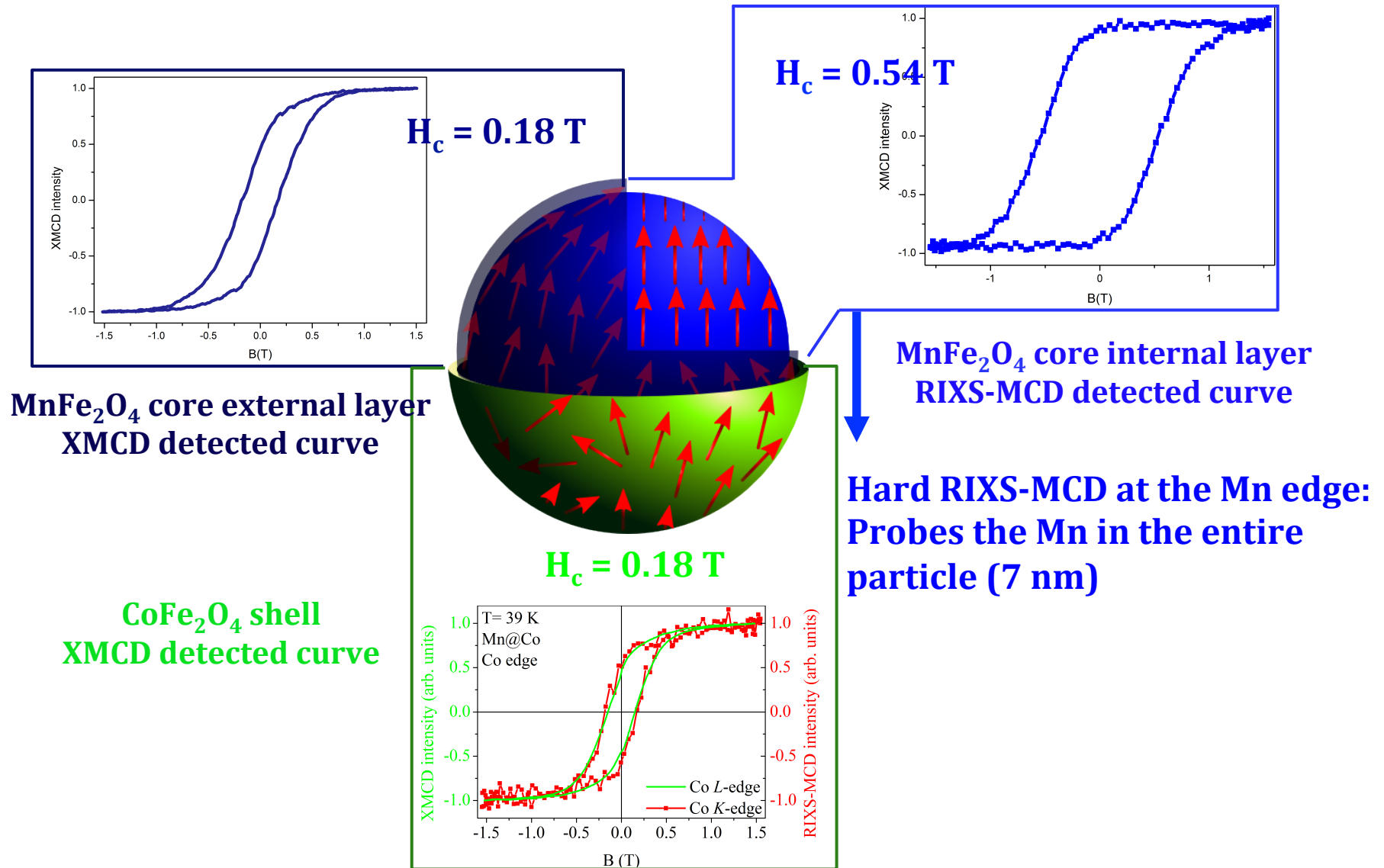


$H_c = 0.18 \text{ T}$

CoFe_2O_4 shell
XMCD detected
magnetization curve

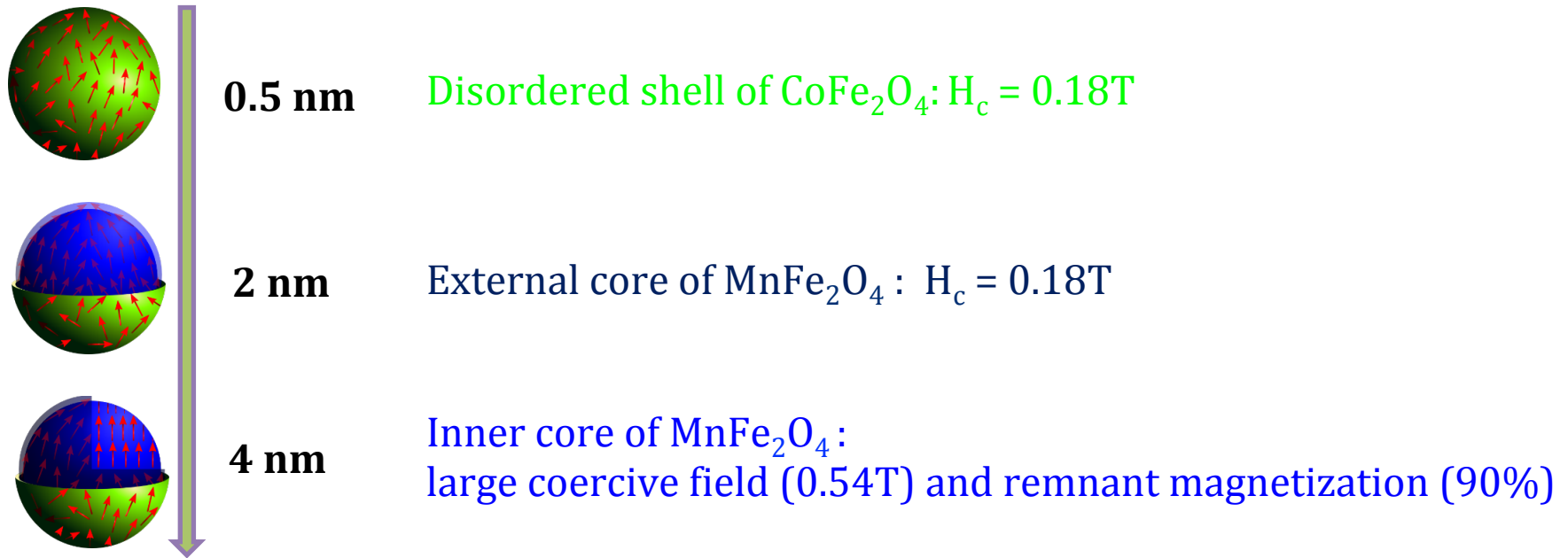


Example 2. Magnetic anisotropies in bimagnetic core@shell particles



Example 2. Magnetic anisotropies in bimagnetic core@shell particles

Distribution of magnetic anisotropies in $\text{MnFe}_2\text{O}_4@\text{CoFe}_2\text{O}_4$



From TEM-EELS and x-ray measurements :

- limited interdiffusion and cationic rearrangement
- ferromagnetic coupling between core and shell

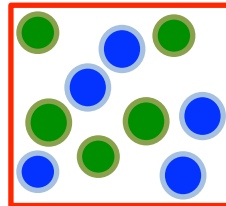
→ Emergent interface-driven magnetic properties of the core

Example 3. Magnetic anisotropies in binary ferrofluids

Most investigations have been so far performed on **size bidispersed** ferrofluids

Binary ferrofluids offer a much larger interplay of dipole-dipole interactions:

= a physical mixture of two ferrofluids with different magnetic anisotropies

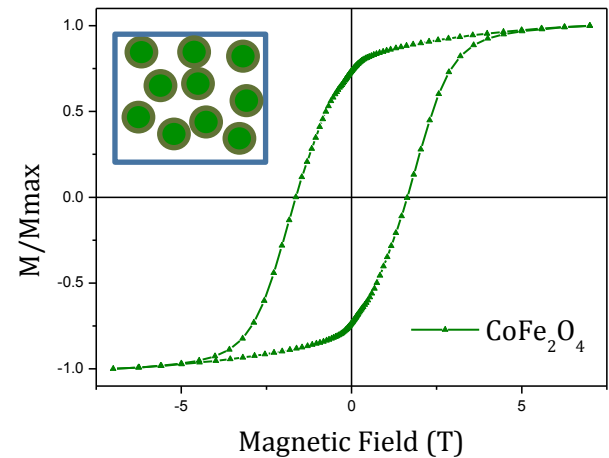
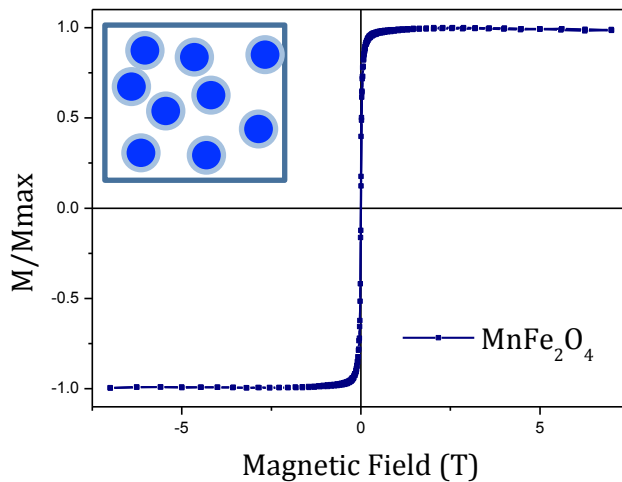
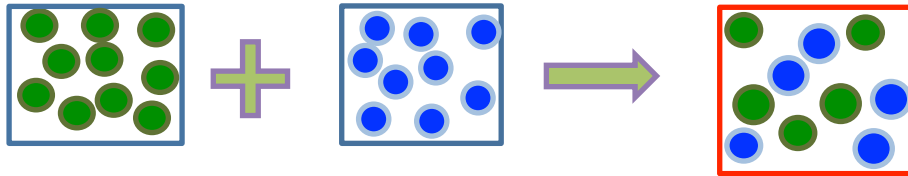


→ Combined with the effect of particle size, shape, and core@shell structuration

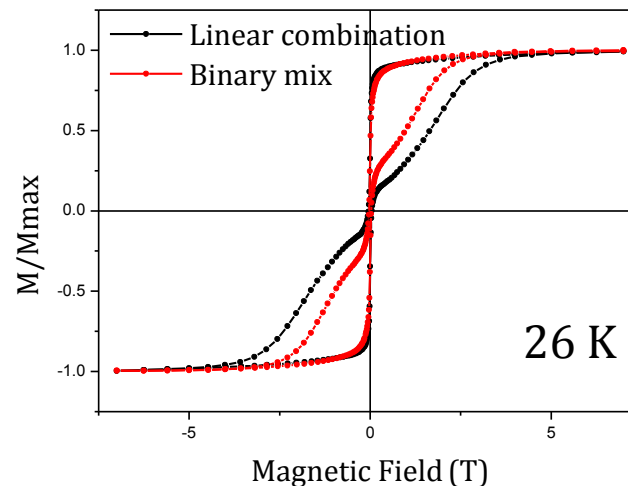
What is the influence of interparticle interactions on magnetic properties ?

Example 3. Magnetic anisotropies in binary ferrofluids

CoFe_2O_4 (6nm) - MnFe_2O_4 (6 nm) binary ferrofluid (1:1, 0.1 % vol.)



Magnetization curve of the binary is not the average of those for the pure components



Example 3. Magnetic anisotropies in binary ferrofluids

What is the influence of interparticle interactions on magnetic properties ?

Element-selective techniques are needed to understand the role of each component

Particle surface and interparticle interactions must be preserved:

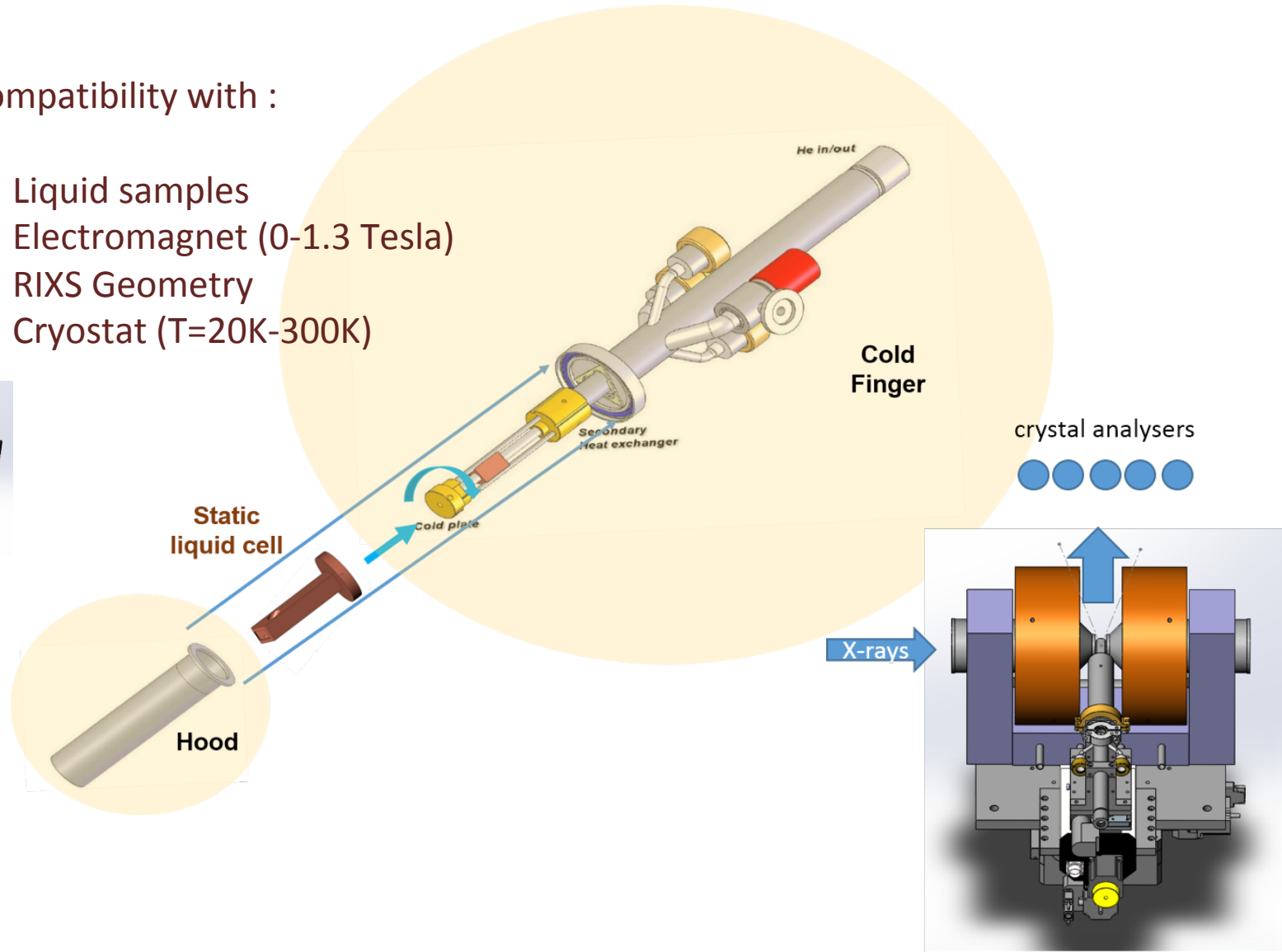
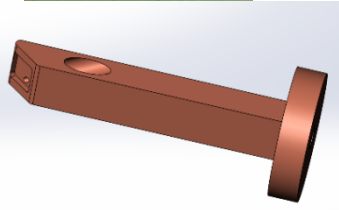
→ Ferrofluids must be investigated as liquid or frozen phases

A static liquid cell for Hard X-ray RIXS-MCD



Compatibility with :

- Liquid samples
- Electromagnet (0-1.3 Tesla)
- RIXS Geometry
- Cryostat ($T=20\text{K}-300\text{K}$)

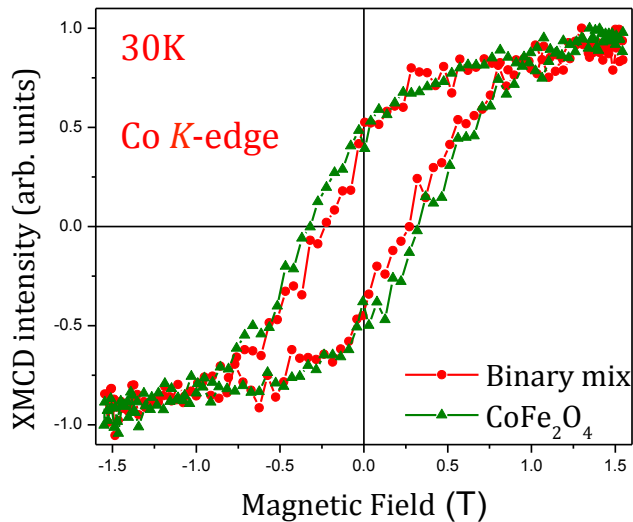


Example 3. Magnetic anisotropies in binary ferrofluids

What are the magnetic properties beyond the average picture ?

Element-selective magnetization curves measured by RIXS-MCD at 30 K (frozen phase)

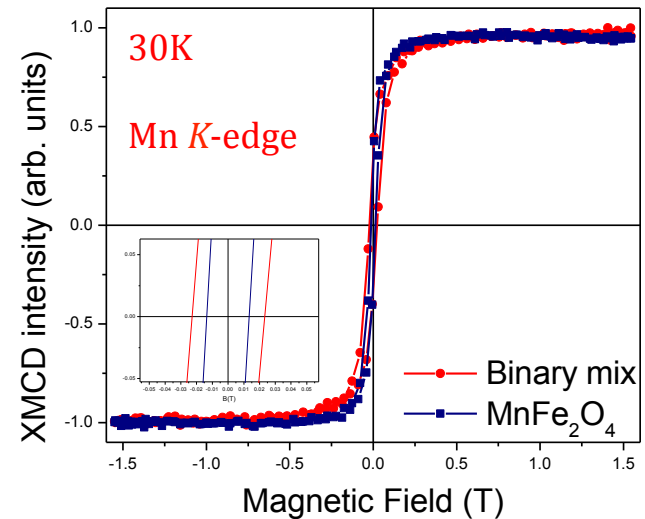
Seen from CoFe_2O_4



CoFe_2O_4 :

magnetic coercivity is **30 % smaller**
in the binary ferrofluid

Seen from MnFe_2O_4



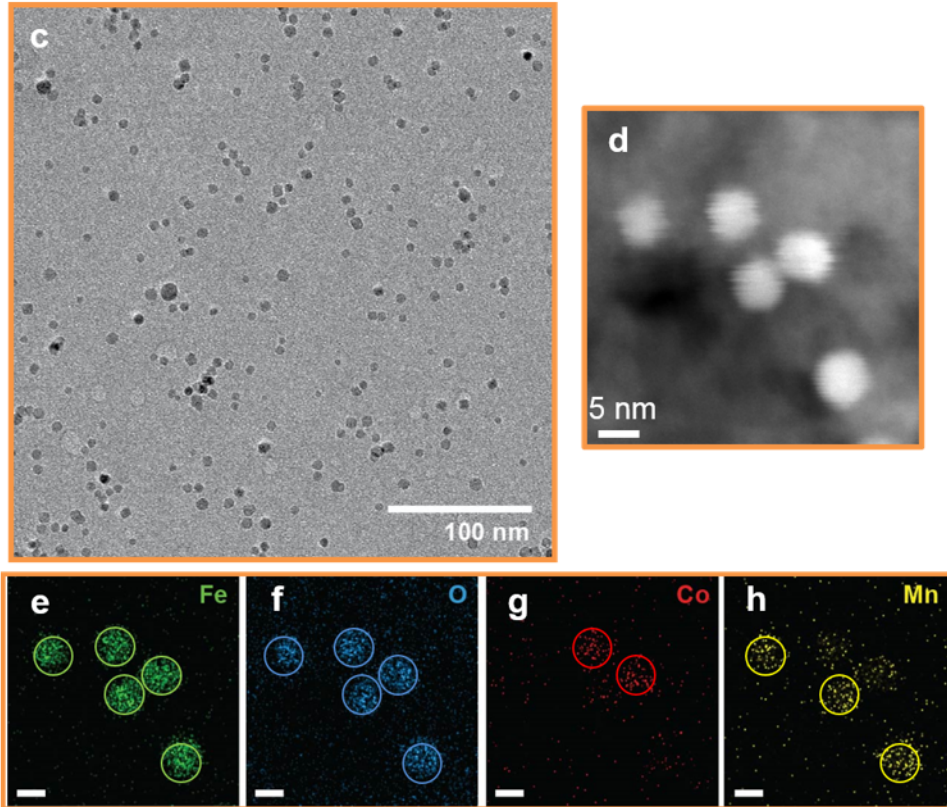
MnFe_2O_4 :

magnetic coercivity is **40% larger**
in the binary ferrofluid

Do interparticle interactions drive the modification of magnetic properties ?

Cryogenic Transmission Electron Microscopy with EDX analysis

Binary ferrofluid



TEM: J. Zecevic (Utrecht University)

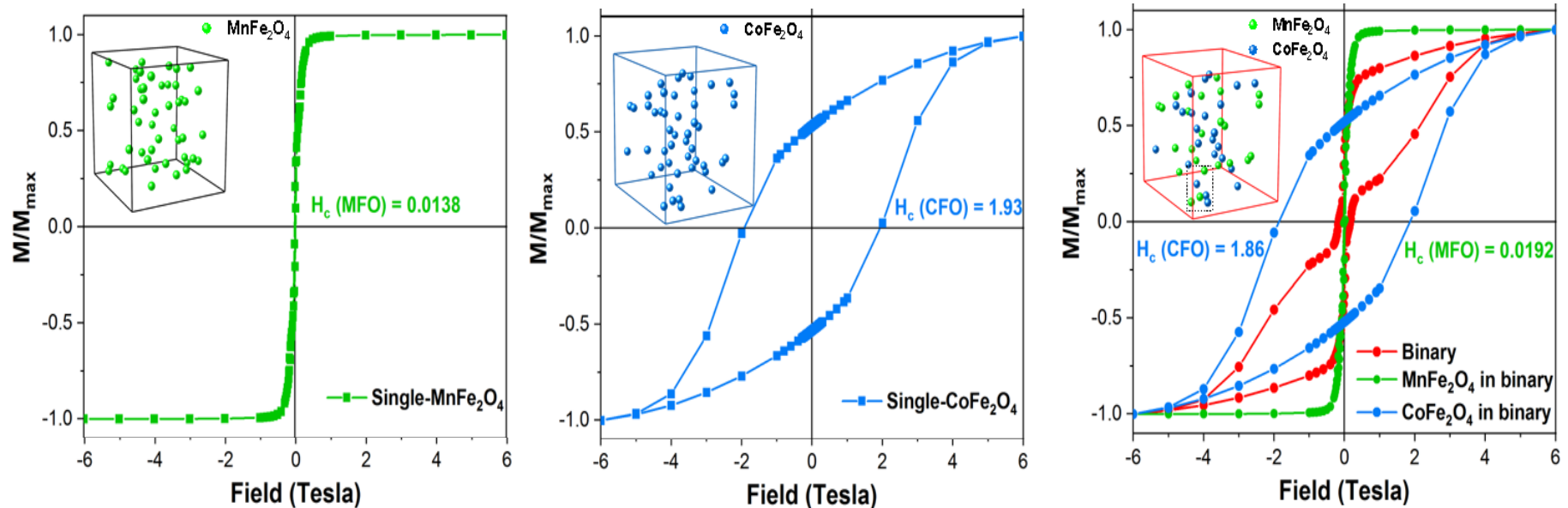
Evidence of neighbouring MnFe_2O_4 and CoFe_2O_4 particles in small clusters despite the very low particle concentration

Do interparticle interactions drive the modification of magnetic properties ?

Monte-Carlo simulations of magnetic properties

Coll. : K. Trohidou (Athens Univ.)

Model : 50 particles dispersed heterogeneously based on TEM images



MnFe_2O_4 : magnetic coercivity is **40% larger** in the binary

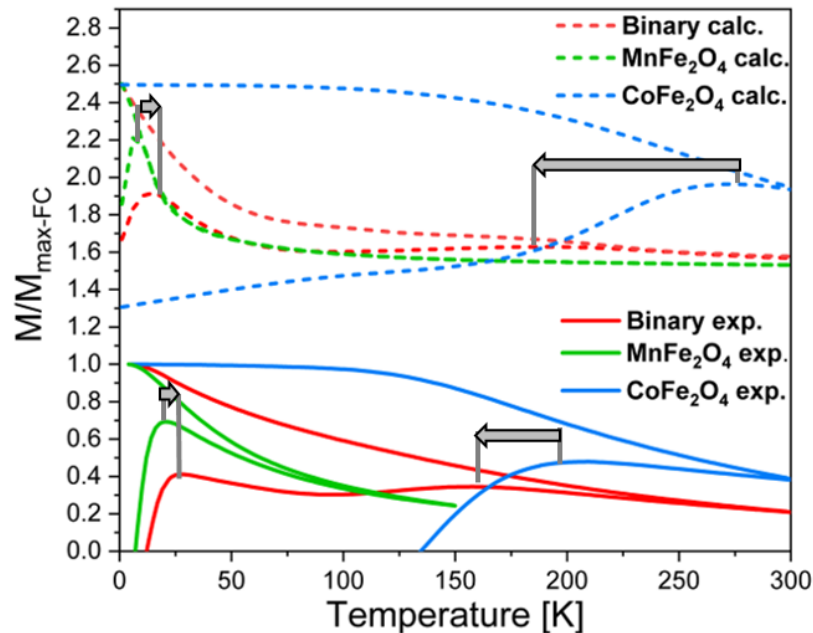
CoFe_2O_4 : magnetic coercivity is **5 % smaller** in the binary

→ consistent with the results of RIXS-MCD detected curves

Do interparticle interactions drive the modification of magnetic properties ?

Monte-Carlo simulations of magnetic properties

Coll. : K. Trohidou (Athens Univ.)



The magnetic properties of the binary are qualitatively reproduced **only** when accounting for clusters involving CoFe_2O_4 and MnFe_2O_4 neighbouring particles

→ a direct relation between the nanoscale interparticle interactions and the modification of macroscopic magnetic properties

Conclusion and prospects

- The **combination of surface- and bulk sensitive x-ray magnetic measurements** provides the distribution of magnetic anisotropies and the internal structure of core@shell bimagnetic particles.
- **Element specific magnetization curves** in a binary ferrofluid allow disentangling the contribution of both magnetic components and revealing their interaction.
- RIXS-MCD with hard x-rays and custom made liquid cell offers new possibilities to investigate magnetic liquids where **interparticle interactions and particle surface have been preserved**.
- Current work on **self-assembled ferrofluids** showing particle assemblies that strongly affect their magnetic properties

Acknowledgements

Dr Niéli Daffé (now in Swiss Light Source)

Dr Nadejda Bouldi (now in Heidelberg)



M. Sikora



AGH

UNIVERSITY OF SCIENCE AND TECHNOLOGY

J. Zecevic

Cryo-TEM



Universiteit Utrecht

Beamtime
Instrumentation

Synthesis
Magnetometry

X-ray spectroscopies



J. Nogués



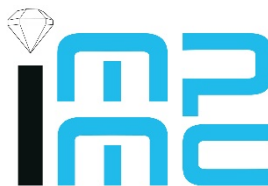
S. Neveu
V. Dupuis



The European Synchrotron



F. Choueikani
Ph. Ohresser



Ph. Saintavit, M.-A. Arrio

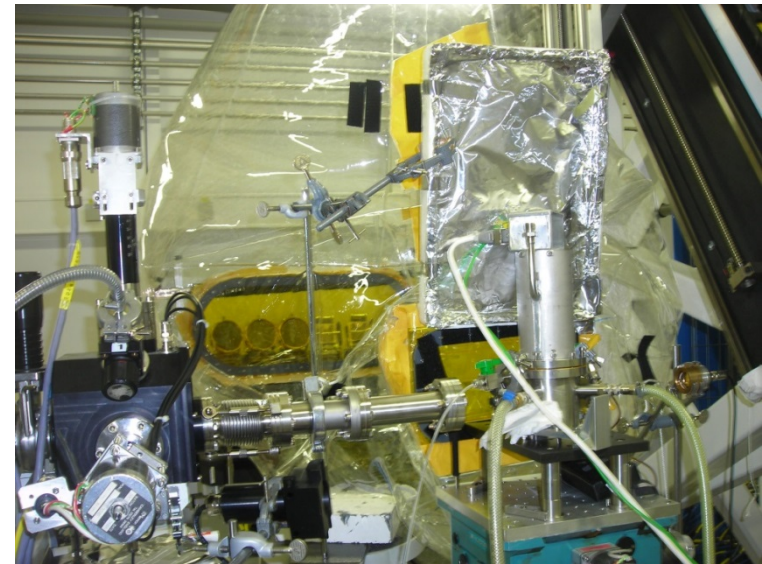
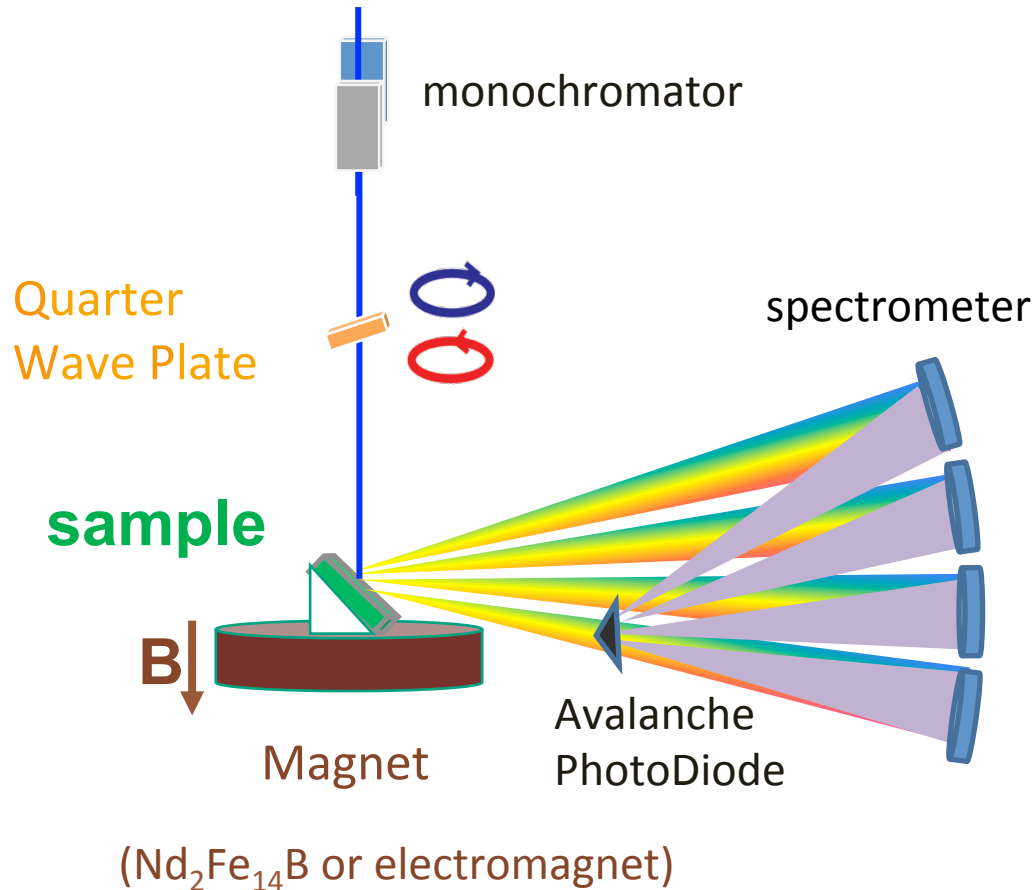
Funding: SOLEIL, Agence Nationale de la Recherche, CNRS, Sorbonne Université



**The final word,
using self-assembled 20 nm nano-flowers:**

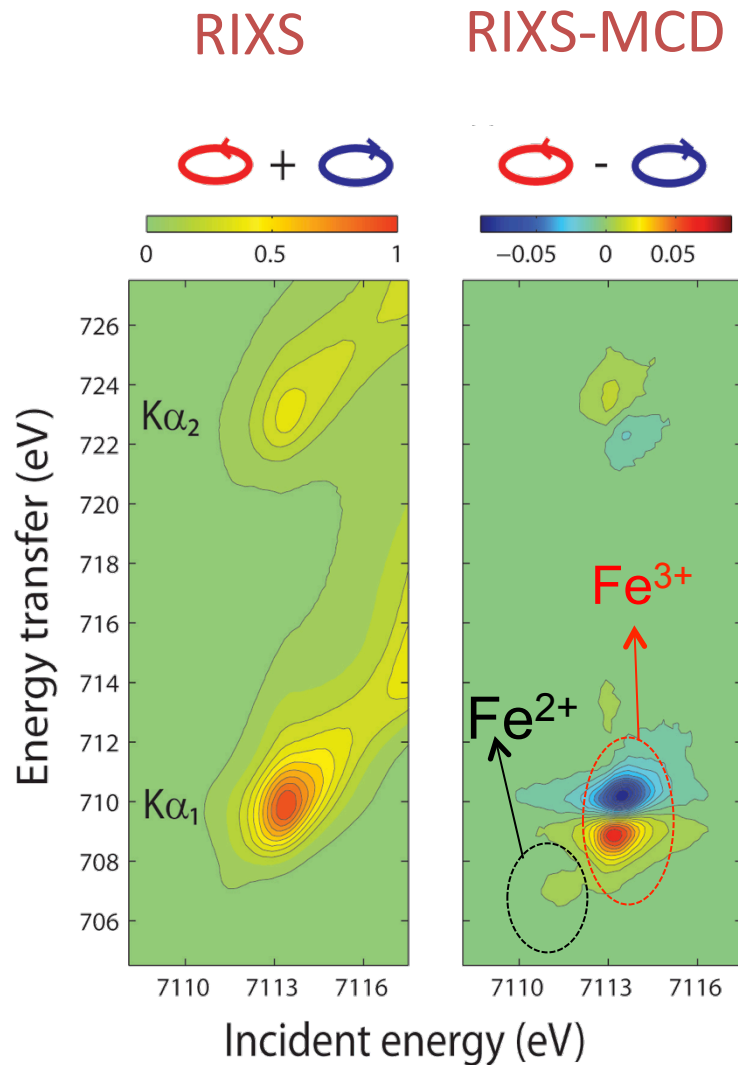


A RIXS-MCD endstation



ID26@ESRF in 2009
GALAXIES@SOLEIL in 2014

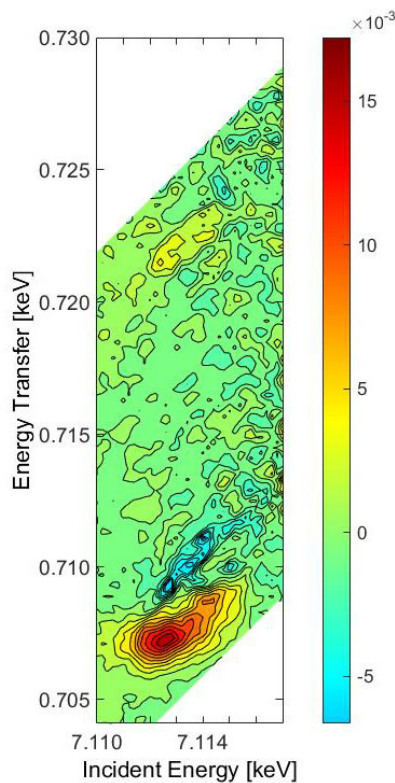
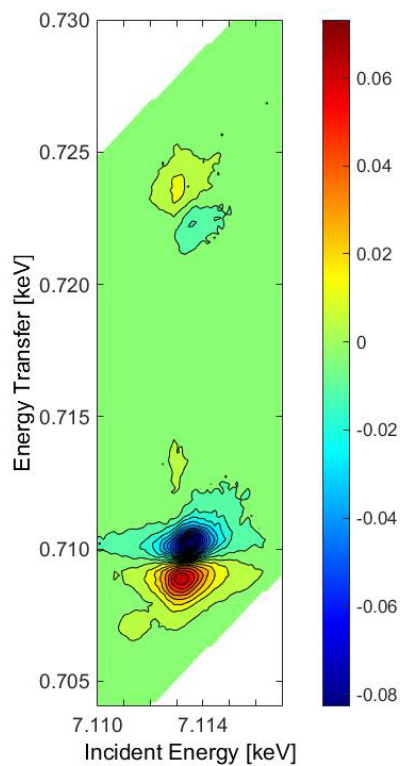
What kind of spectroscopic information can be extracted ?



Fe *K* pre-edge in $Fe^{2+} Fe^{3+}_2 O_4$

- Valence of absorbing ion

What kind of spectroscopic information can be extracted ?

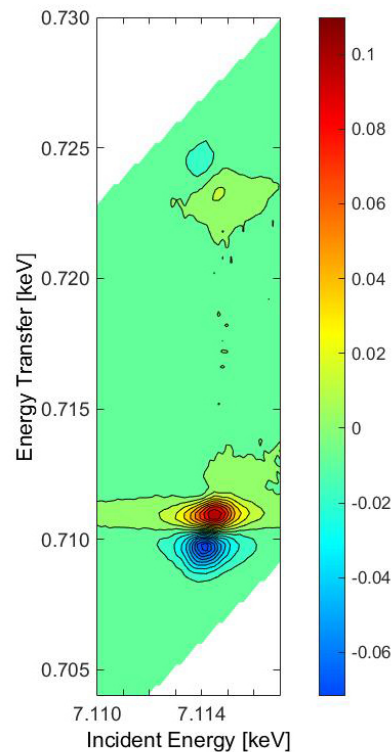
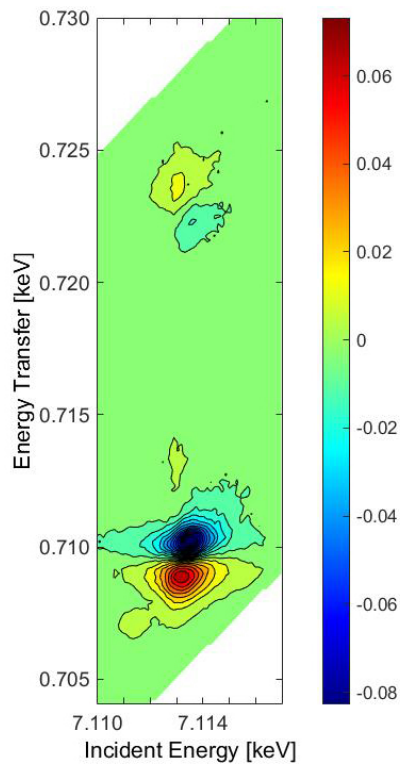


- Valence of absorbing ion
- Coordination of absorbing ion:

Tetrahedral (RIXS-MCD = 15-20 %)

Octahedral (RIXS-MCD = 2-5 %)

What kind of spectroscopic information can be extracted ?

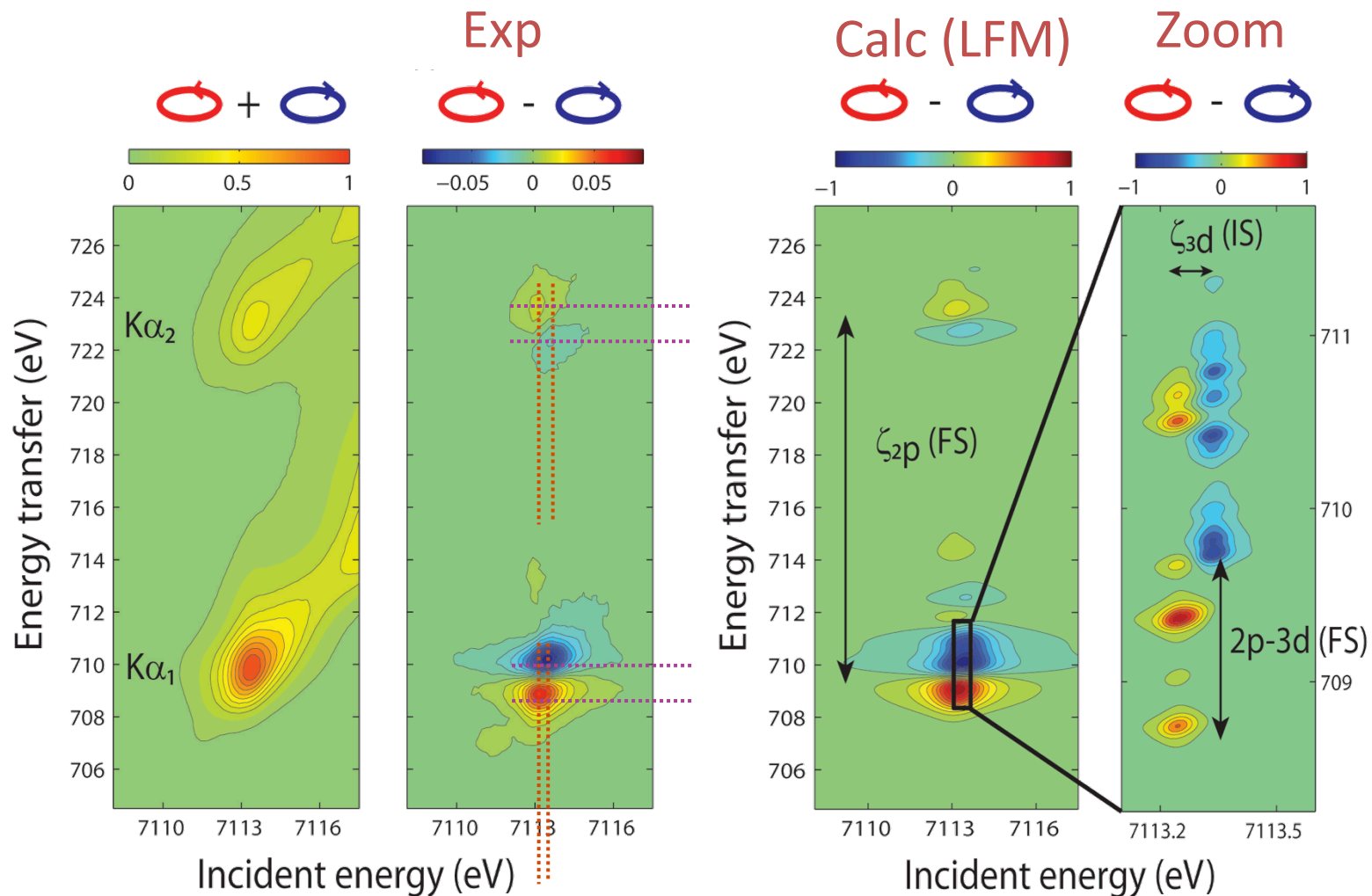


- Valence of absorbing ion
- Coordination of absorbing ion
- Orientation of magnetic moment:

Antiparallel or parallel
to external magnetic field

What kind of spectroscopic information can be extracted ?

Energy splittings are related to interactions in intermediate state (IS) and final state (FS)



1s2p RIXS-MCD in Fe oxides

$T_d + O_h$ sites

O_h sites

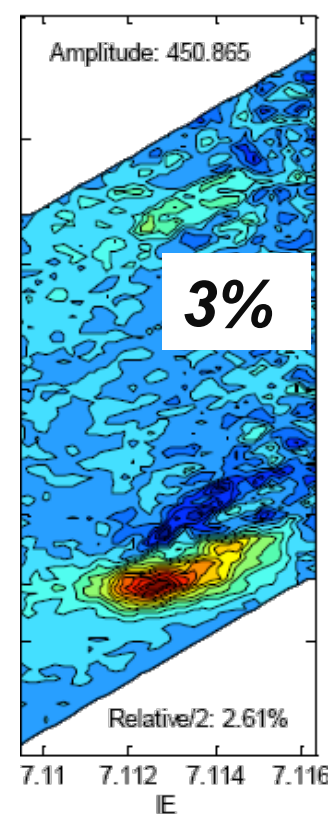
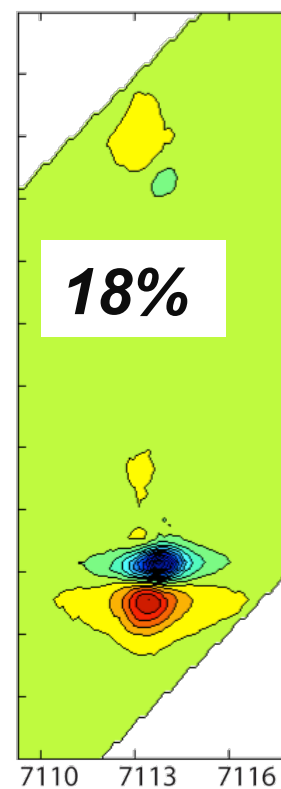
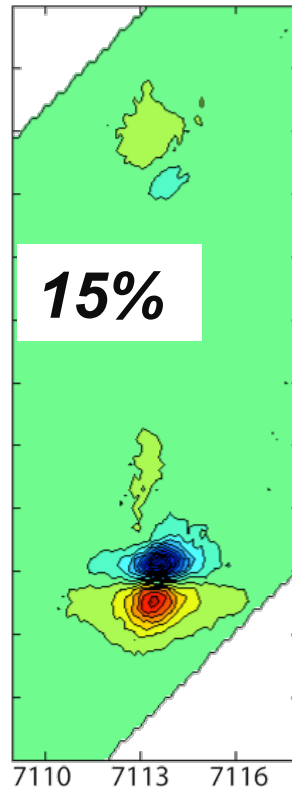
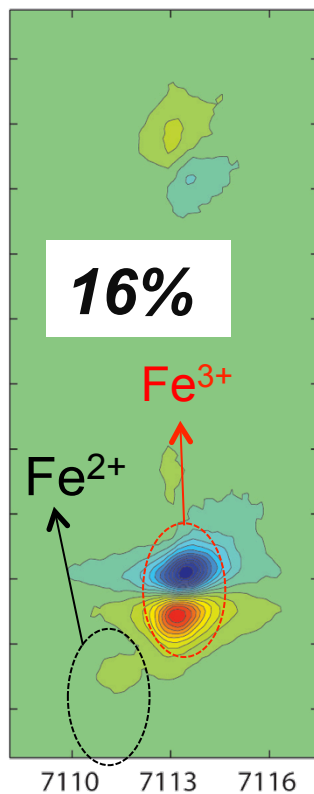
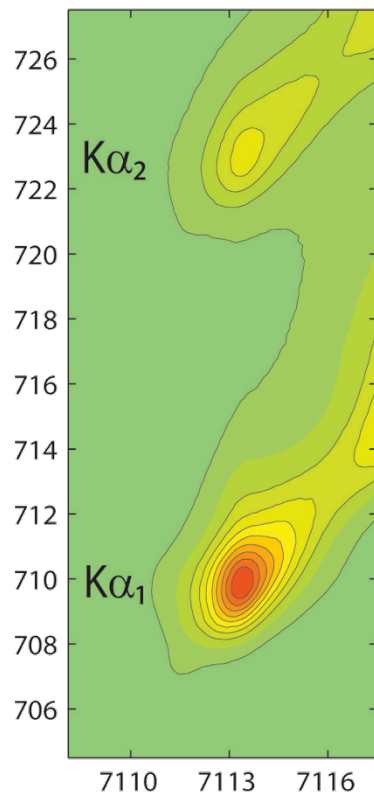
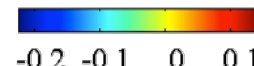
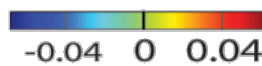
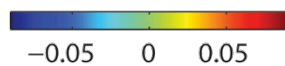
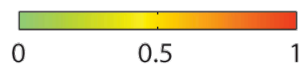
Fe K pre-edge in:

$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$

$\text{CoFe}^{3+}_2\text{O}_4$

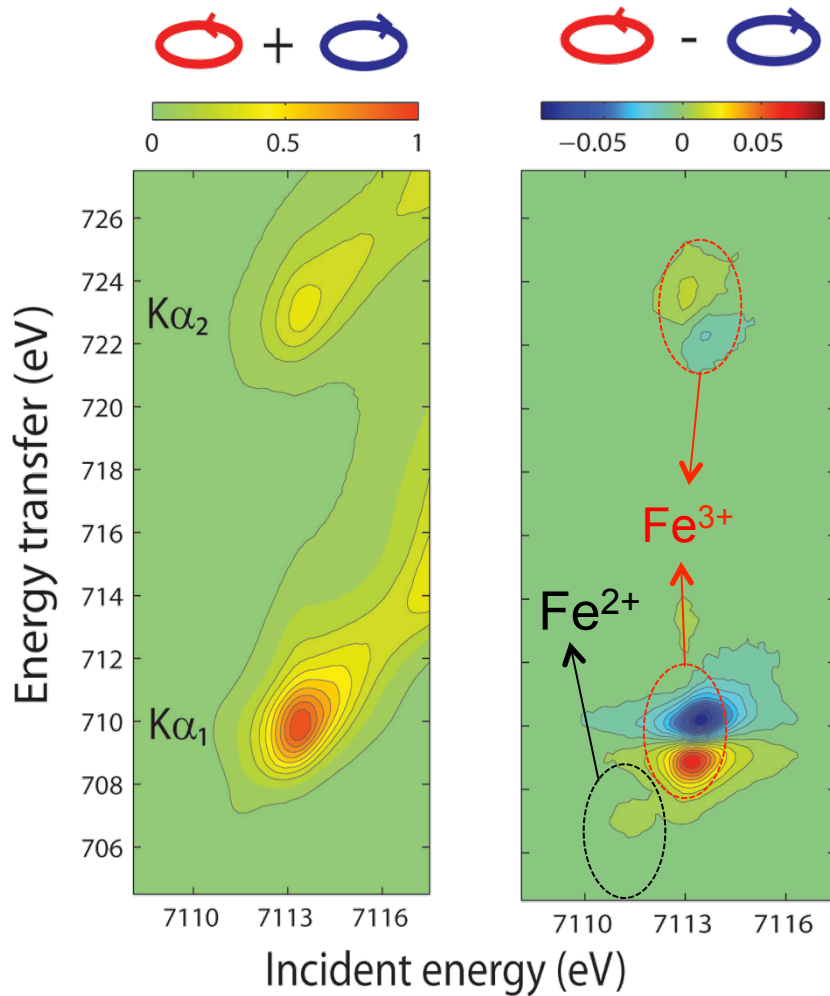
$\text{Y}_3\text{Fe}^{3+}_5\text{O}_{12}$

$\text{Sr}_2\text{Fe}_{(O_h)}\text{ReO}_6$



Incident energy (eV)

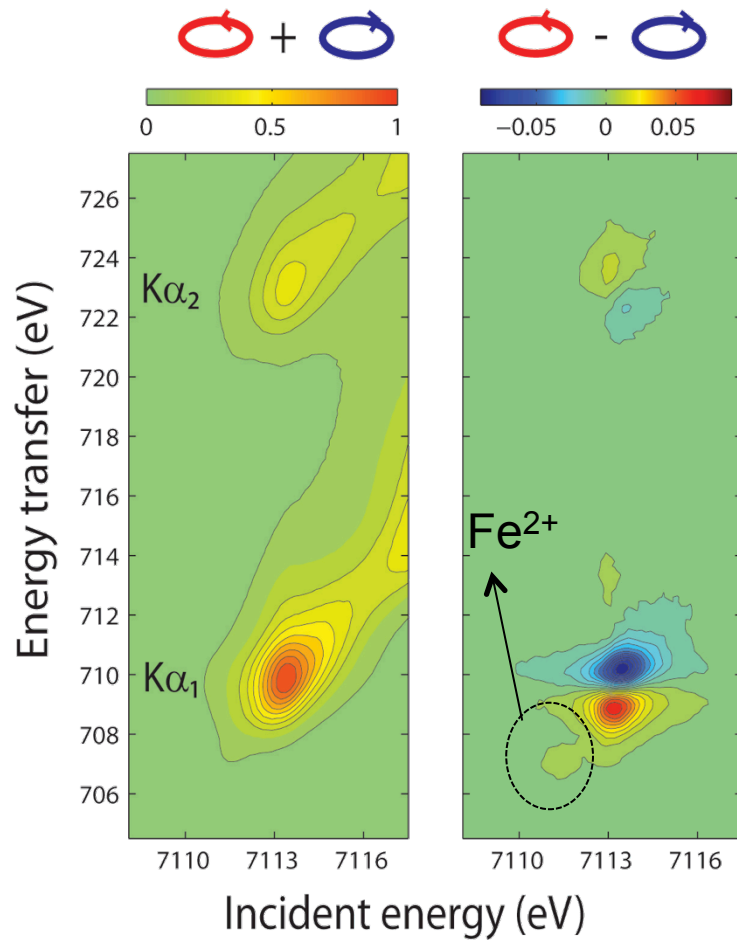
1s2p RIXS-MCD at the Fe K edge in Fe_3O_4



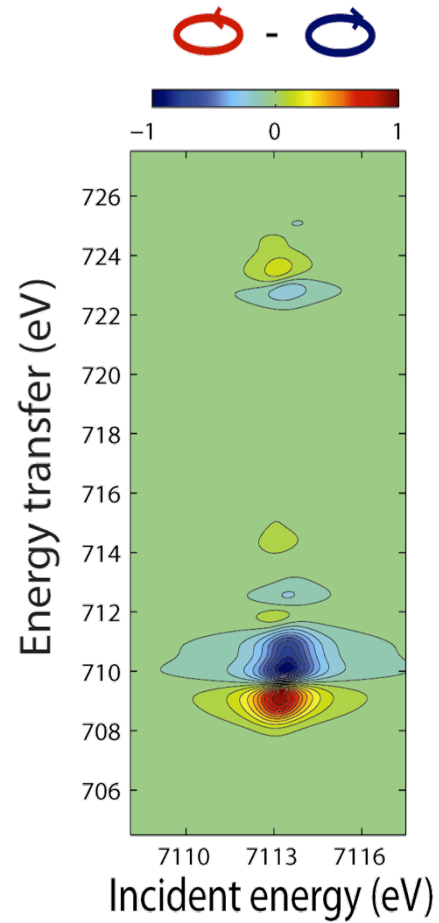
A 2D mapping of magnetic signatures

better separation

Exp Fe_3O_4



Calculation $\text{Fe}^{3+}(\text{T}_d)$

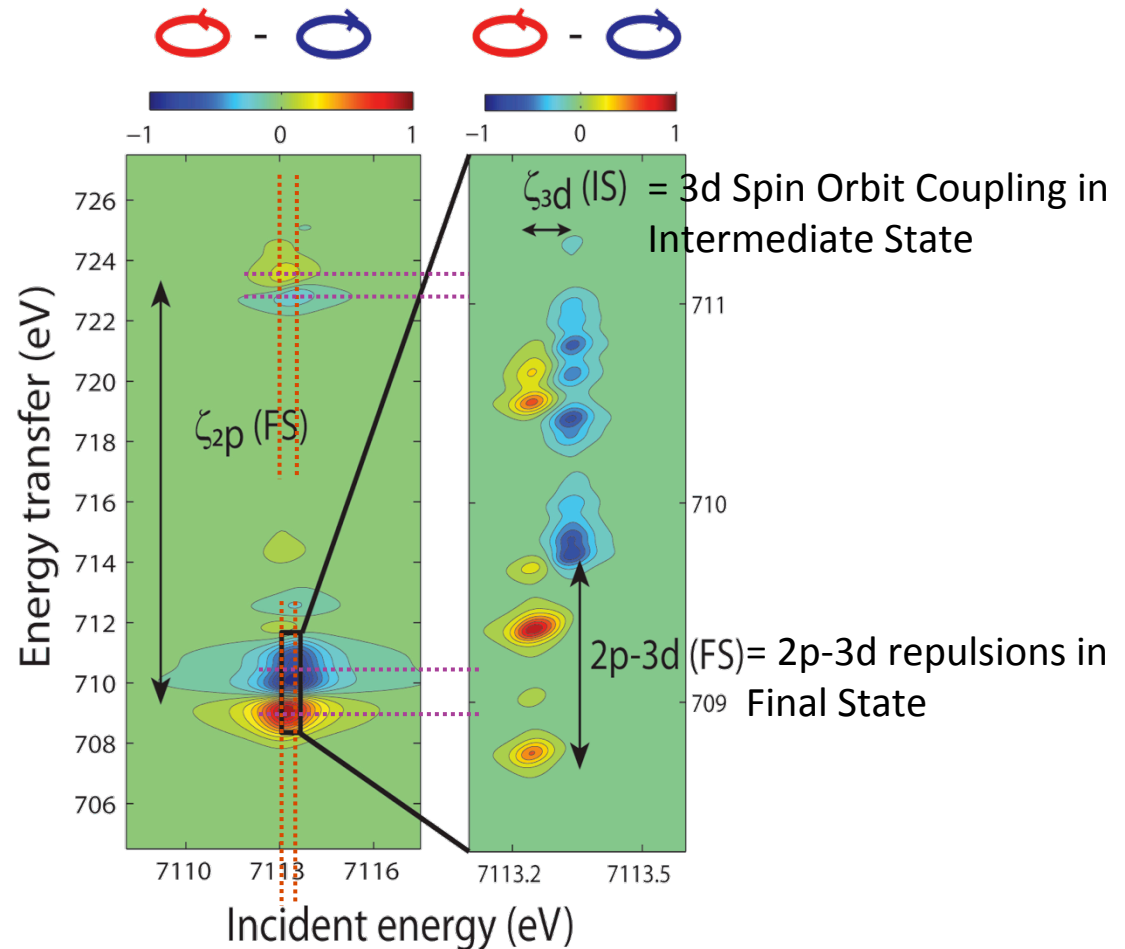


M. Sikora, A. Juhin, TC Weng, P Saintavit, C Detlefs, F De Groot, P Glatzel,
Phys. Rev. Lett. 105, 037202 (2010)

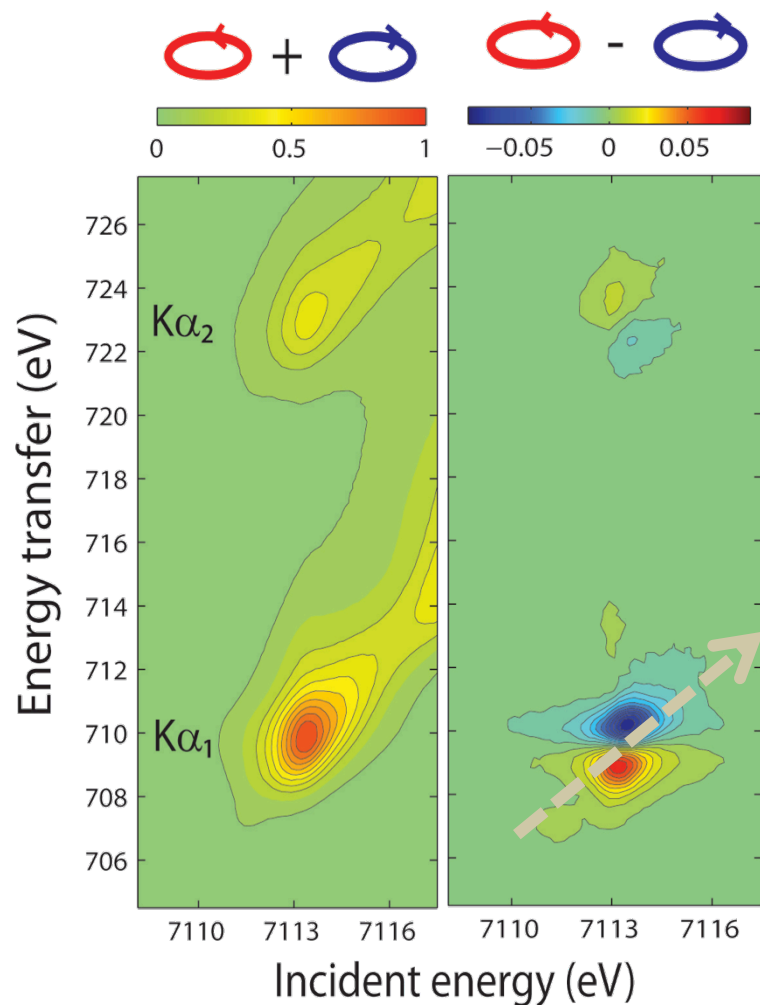
Origin of the RIXS-MCD effect

Calc (Ligand Field Multiplet theory)

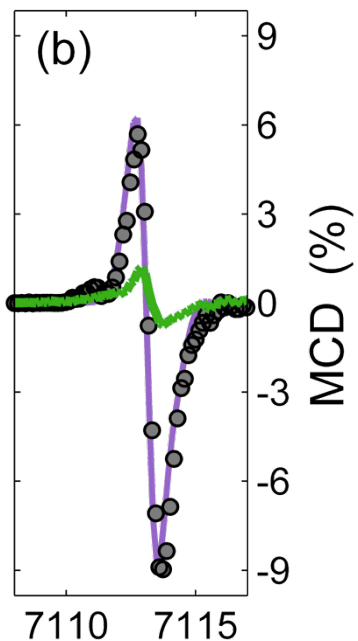
The RIXS-MCD intensity enhancement is a result of both reduced lifetime broadening and increased splitting in the $2p^5 3d^{n+1}$ final state



Comparison to *K*-edge XMCD

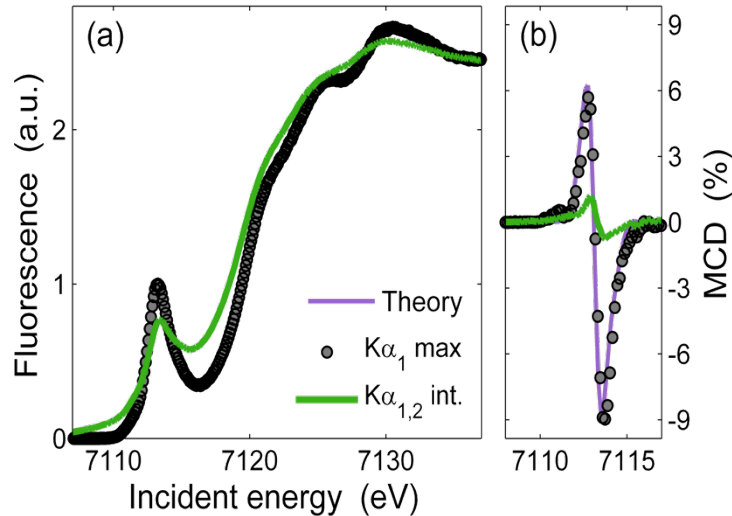
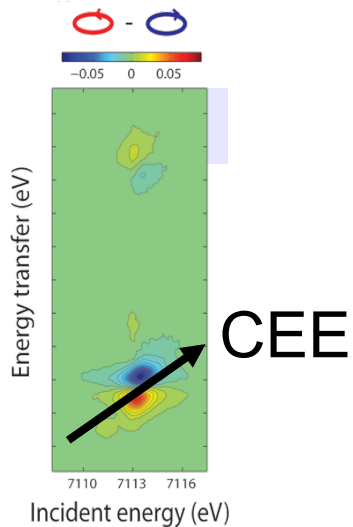


— Theory
— Total Fluorescence Yield
● CEE scan from RIXS-MCD



- Sharper XMCD signal
 $\Gamma_{\text{CEE}} \approx \Gamma_{2p}$
- XMCD multiplied by 10

RIXS-MCD: Line scans



Comparison to K-edge XMCD

- Spectral features are sharper
- XMCD detected by RIXS:
gain of factor of 10



*Can be further improved if
experimental resolution is improved*

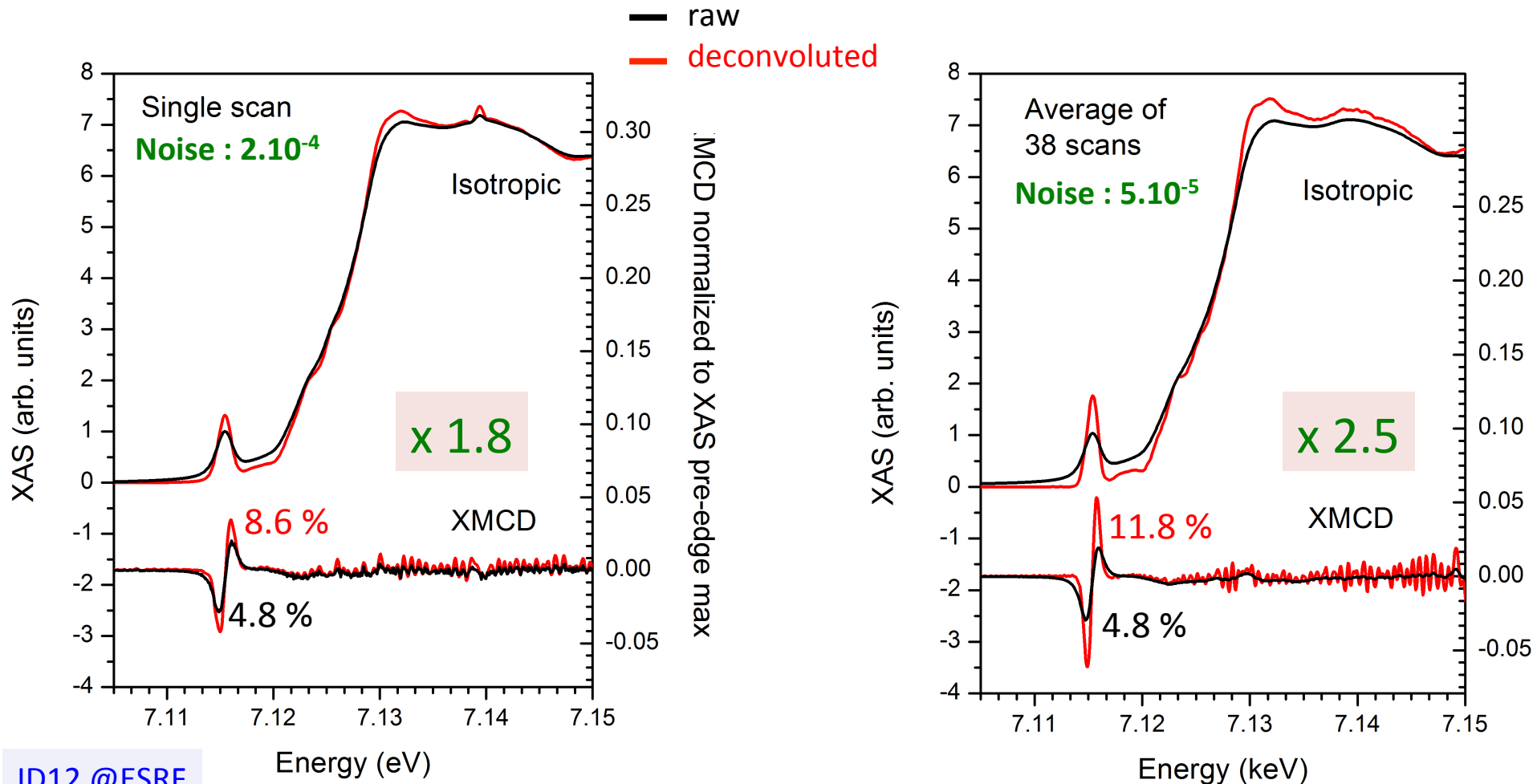
Comparison to L-edge XMCD

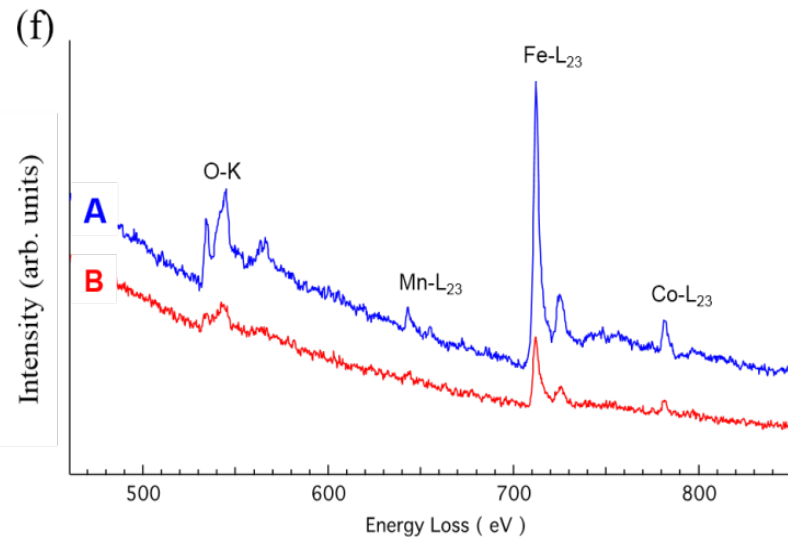
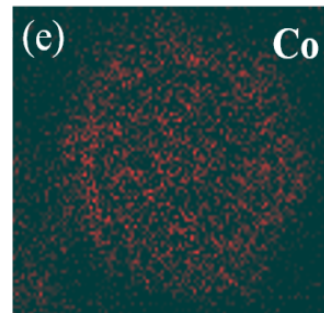
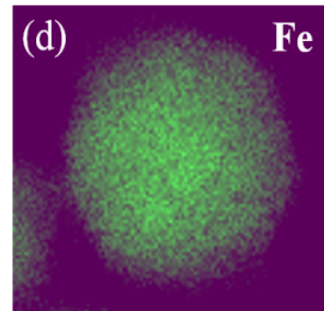
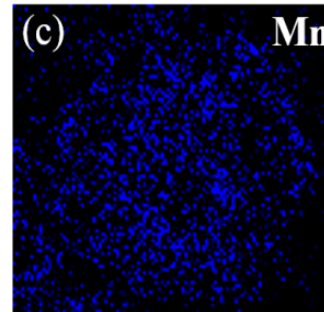
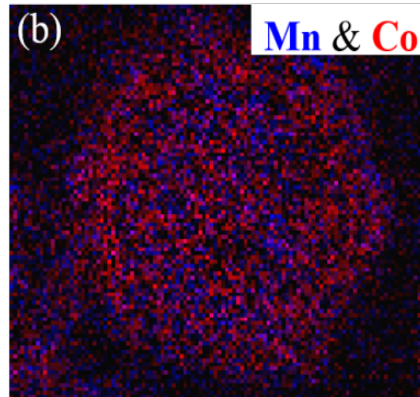
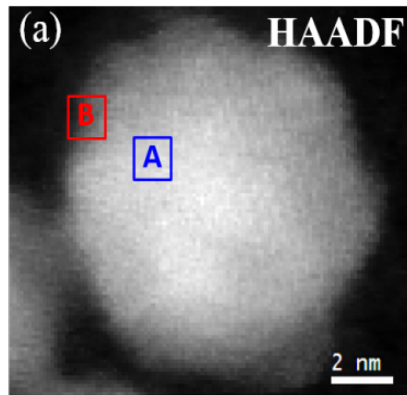
- Same order of magnitude
- Here, the contribution of tetrahedral Fe^{3+} is dominant

Comparison to *K*-edge XMCD

High quality XMCD spectra measured in Total Fluorescence Yield

Partial deconvolution from 1s corehole lifetime broadening (DECONV-GNXAS)





A. Gloter (LPS Orsay, France)

From TEM-EELS and XAS/XMCD/RIXS-MCD spectra :

- limited interdiffusion and cationic rearrangement
- Ferromagnetic coupling between core and shell